NOTE OF EXPLANATION FOR AQUATIC FACT SHEETS FOR ZINC

The Aquatic Type numerical values for zinc are supported by more than one Fact Sheet. The freshwater acute value is supported by the Fact Sheet dated March 1998. The freshwater chronic value and both saltwater values are supported by the Fact Sheet dated December 2, 1993. The reader should disregard the documentation for the freshwater acute value in the December 2, 1993 Fact Sheet.

-- NYSDEC 3-98

Fact Sheet Date: DEC 2 1993

- AQUATIC RESOURCE FACT SHEET -
- Ambient Water Quality Value -

SUBSTANCE(S): *ZINC, Dissolved*

CAS REGISTRY NUMBER(S): NA

BASIS	VALUE (ug/L) FRESHWATER	SALTWATER
Fish Propagation, Survival	*	66
Fish Survival	**	95

REMARKS:

* exp (0.85 [ln (hardness mg/l)] + 0.50)

** exp (0.85 [ln (hardness mg/l)] + 0.86)

SUMMARY OF INFORMATION:

The International Joint Commission (IJC 1977) recommended a zinc criterion of 30 ug/l total zinc in an unfiltered water sample to protect aquatic life. The criterion was based on an estimated "safe concentration" for fathead minnow reproduction between 27.3 and 30 ug/l. In the study cited, copper and cadmium were also present at chronic threshold levels. IJC (1986) has proposed amending the zinc criterion, reducing it from 30 to 10 ug/l in order to prevent toxicity to phytoplankton. IJC concluded that in the absence of complexing agents, zinc could inhibit phytoplankton growth at as low as 15 ug/l. IJC also concluded that a criterion of 30 ug/l would be adequate to prevent toxicity to fish, but noted that fish have been found to avoid zinc as low as 5.6 ug/l at a hardness of 13-15 mg/l.

Because of the variability of zinc toxicity in different waters, EPA (1976) issued a narrative criterion to derive site-specific values. They recommended a freshwater value of 0.01 times the 96-hour LC50 as determined through bioassay using a sensitive resident species. EPA stated that the same criterion should also protect the marine environment.

EPA issued revised zinc criteria in 1980. For total recoverable zinc, the criterion to protect freshwater aquatic life was recommended as 47 ug/l as a 24-hour average and the concentration should not exceed the numerical value given by exp (0.83 [ln (hardness)] + 1.95) at any time. For example, at hardnesses of 50, 100, and 200 mg/l as $CaCO_3$ the concentration of total recoverable zinc should not exceed 180, 320 and 570 ug/l, respectively, at any time. For total recoverable zinc, the recommended criterion to protect saltwater aquatic life was 58 ug/l as a 24-hour average and the concentration should not exceed 170 ug/l at any time. In its data summary, EPA (1980) reported a toxicity value less than the freshwater 24-hour average criterion. A 10-day LC50 for a midge was 37 ug/l at 47 mg/l hardness.

Recently, EPA (1987) issued its latest revision of the zinc criteria. In freshwater, the 4-day average should not exceed the numerical value (in ug/l) given by exp (0.8473 [ln (hardness)] + 0.7614), and the 1-hour average should not exceed the numerical value (in ug/l) given by exp (0.8473 [ln (hardness)] + 0.8604). At hardnesses of 50, 100 and 200 mg/l as $CaCo_3$, the 4-day average criteria are 59, 110 and 190 ug/l, respectively, and the 1-hour average criteria are 65, 120 and 210 ug/l, respectively. In saltwater, the 4-day average should not exceed 86 ug/l and the 1-hour average should not exceed 95 ug/l. EPA recommended at that time that all zinc criteria should be expressed as total recoverable until an analytical method such as acid-soluble is approved. Also, the allowable exceedance frequency for criteria should not be more than once every 3 years to allow ecosystems sufficient time to recover from excursions above criteria.

EPA (1987) reviewed a great deal of literature on zinc toxicity to aquatic plants and noted some studies which show adverse effects at concentrations lower than the recommended criteria. No criterion to protect aquatic plants was derived, however. It appears from their review that because of the great range of sensitivity of algae, a criterion to protect aquatic plants could not be appropriately derived.

DEC submitted comments (August 27, 1986) to EPA on the proposed zinc criteria which EPA had made available for public comment on May 28,1986 (Fed. Reg. 51: 19269). DEC questioned the rationale for using only four of the species acute to chronic ratios and a chinook salmon ratio of less than one to calculate a final acute to chronic ratio. EPA did not respond to the use of the chinook salmon ratio but explained that ratios for "flagfish, brook trout, and fathead minnow were not used because they are not very sensitive species, and sensitive species often have lower acute to chronic ratios than resistant species." (Fed. Reg. 52(40:6219). The EPA argument about acute to chronic ratios is not convincing. Flagfish can be excluded, not because of its insensitivity as EPA asserts, but because its acute to chronic ratio is greater than a factor of 10 above the acute to chronic ratios for sensitive species. NYS disagrees with EPA, however, on the issue of the sensitivity of fathead minnow. NYS judges fathead minnow sensitivity in this dataset to be in the same range of sensitivity as the four other most sensitive genera and, therefore, warrants inclusion in the calculation of the final acute to chronic ratio. For chinook salmon, a ratio of one should be used because it is toxicologically illogical to use an acute to chronic ratio less than one.

Excluding the sockeye salmon ratio because it is a "less than" value, using the geometric mean of the three Daphnia ratios, and using a chinook salmon ratio of one, the geometric mean of these values and the remaining sensitive species ratios (rainbow trout, fathead minnow and Mysidopsis bahia) results in a final acute to chronic ratio of 2.9.

EPA (1976) cited reports that the mean zinc value in U.S. waterways was 64 ug/l, with a maximum of 1,183 ug/l in freshwater and a maximum in seawater of 10 ug/l. IJC (1986) cited reports of ranges of zinc concentrations in Lakes Erie and Ontario of 0.55-24 ug/l and 1-13 ug/l, respectively. They concluded that improved analytical procedures and a reduction in sample contamination decreased substantially the estimates of background levels of zinc in the Great Lakes. EPA (1987) cited reports that zinc in uncontaminated freshwater typically ranges from 0.5 to 10 ug/l and in clean seawater it ranges from 0.002 to 0.1 ug/l. DEC (1986) summarized toxics monitoring throughout NYS in 1985, including total recoverable zinc measurements. Many of the waters sampled were in excess of the zinc detection limit of 20 ug/l, but most were less than 100 ug/l. In freshwater, most values greater than 100 ug/l were found in November. In saltwater, 6 of 7 stations exceeded 100 ug/l at some time, but all 7 stations are located in known polluted waters in New York City. DEC (1986) cautioned that reported zinc levels could be elevated due to contamination in the collection and analytical procedures, and that the zinc data should be regarded with some skepticism.

It has been shown that zinc is most often found as inorganic forms in fresh- and saltwater (Nelson and Donkin 1985). A few studies have indicated that organic and inorganic complexes of zinc may be slightly toxic (Starodub et al., 1987). Other investigators have reported on studies indicating, however, that zinc precipitates were not toxic to fish (Bradley and Sprague 1985).

EPA (1987) recognized the importance of the form of zinc relative to its toxicity. In freshwater, as pH varies from 6.0 to 9.0, the free zinc ion varies from 98% to 6%. In saltwater, at pH 7 the free ion comprises 50% of the dissolved zinc species. EPA concluded that among hardness, alkalinity and pH, hardness was the best water quality characteristic to reflect variation in zinc induced toxicity. EPA stated that zinc sorbed to solids and some zinc complexes probably have lower toxicities to some animals and plants, but may be toxic to animals which feed on the particles containing zinc. EPA noted that some complexed forms, such as zinc-EDTA, are probably very low in most natural waters. EPA (1987) concluded that the acid-soluble measurement is probably the best estimate of forms of zinc in natural surface waters that are or could readily become bioavailable.

As EPA (1987) noted, zinc-organic complexes can reduce zinc toxicity. Gauss and Winner (1985) found that addition of 1.5 mg/l humic acid raised the Daphnia no-effect concentration from 25 to 100 ug/l in soft water and 179.2 to 225 ug/l in hard water. Some ligands may form stronger complexes than others which could affect the degree of mitigation of zinc toxicity. Nor and Cheng (1986) found that EDTA and humic acid inhibited uptake of copper by a plant, but other ligands (fulvic acid, amino acids and simple organic acids) did not inhibit uptake. Chelators often used in laboratory studies, such as EDTA and NTA, may be stronger chelators than natural humic acids (Strumm and Morgan 1981, van den Berg and J.R. Kramer 1979). Landrum et al. (1987) expressed concern that dissolved organic matter could in the short-term reduce bioavailability of organic toxics in the water column, but "would additionally contribute to increased low level exposure to biota due to increased compound dispersal" and cause additional precipitation of toxics at the fresh/saltwater interface in estuaries. Landrum (pers. comm. with P. Landrum, Great Lakes Environmental Research Lab., Ann Arbor, MI) suggests that metals will likely bind more tightly to dissolved organic matter, thereby further reducing short-term bioavailability, but possibly still providing long-term, low-level availability and significant precipitation where fresh and saltwater meet. Rodgers et al. (1984) found that sorption of zinc to suspended solids significantly reduced toxicity to aquatic life. Toxicity mitigation by sorption is probably dependent on other water quality factors. McIlroy et al. (1986) found that zinc sorption to suspended solids decreased from about 60-90% at pH 8 to less than 20% at pH 6. Insoluble metal particles that were thought to exhibit low toxicity have also been found to be toxic. Landis et al. (1986) found that brass dust (copper and zinc alloy) in water impacted Daphnia and algae.

Zinc had been found to accumulate in fish and shellfish. In fresh and saltwater fish, bioaccumulation factors (BF) in whole body ranged from 4-966 with a maximum of 466-966 in guppy; factors for edible fillets of fish are not available. In shellfish, the BF ranged from 4-23,820; the geometric mean was 527 (EPA, 1987). This information indicates the importance of investigating the development of values to protect consumers of fish and shellfish against accumulation of zinc. A separate evaluation and bioaccumulation based value to protect human health should be proposed.

DERIVATION OF STANDARDS:

EPA (1987) provides adequate information to support the derivation of zinc criteria to protect aquatic life accounting for natural variations in hardness. The zinc criteria were published in accordance with Stephan et al. (1985). The EPA one-hour average fresh (a water hardness dependent equation) and saltwater (95 ug/l) criteria are applicable to New York waters and appropriate to provide for survival of fish in classes D and SD, respectively (see page 2, paragraph 2 this document). For reasons discussed above, it is concluded that the EPA four-day average criteria are too high. Using a final acute to chronic ratio of 2.9 the following criteria can be derived:

Freshwater

Final Chronic Value = 130 ug/l (Final Acute Value from EPA, 1987) divided by 2.9 = 45 ug/l, at 50 ppm hardness.

ln (Final Chronic Intercept) = ln (45) - (0.85 x ln 50 ppm) = 0.50.

Formula for Final Chronic Value = exp (0.85 [ln (ppm hardness)] + 0.50)

Examples at 50 ppm hardness, criterion = 46 ug/l
at 100 ppm hardness, criterion = 83 ug/l
at 200 ppm hardness, criterion = 149 ug/l

Saltwater

Final Chronic Value = 190 (Final Acute Value) divided by 2.9 = 66 ug/l.

New York values for zinc should be expressed as dissolved. The most current developments in the science of metals toxicity (see M.G. Prothro, 1993) lead to the understanding that the most toxic forms of zinc to aquatic life are dissolved. Because organic and inorganic complexes of zinc are much less toxic, and because the particulate form is significantly less toxic and less directly available as a toxicant in ambient waters than is zinc in the dissolved form (Eisler, 1993), the dissolved form more accurately estimates the bioavailable toxic fraction.

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DFW/CSS

Fact Sheet Date: March 12, 1998

NEW YORK STATE
- AQUATIC FACT SHEET -

Ambient Water Quality Value for Protection of Aquatic Life

SUBSTANCE: Zinc, dissolved

CAS REGISTRY NUMBER: Not Applicable

TYPE:	BASIS:	FRESHWATER AMBIENT WATER QUALITY VALUE (ug/L):
Acute	Survival	$(0.978)e^{(0.8473[\ln \text{ppm hardness}] + 0.884)}$

INTRODUCTION

This value applies to the water column and is derived to protect aquatic life from the effects of waterborne contaminants. Values for the protection of survival of aquatic life are referred to as Aquatic (Acute) or A(A) values.

SUMMARY OF INFORMATION AND DERIVATION OF VALUE

U.S. EPA (1995a,b) has derived an acute aquatic life criterion for dissolved zinc for the Great Lakes Water Quality Initiative (GLI). The Department has reviewed this criterion and determined that it is based on appropriate data and derived according to the scientific procedures in current and proposed 6 NYCRR Part 702. It is thus determined to be an appropriate ambient water quality value for protection of aquatic life for New York State.

The attachment to this fact sheet provides U.S. EPA's derivation of the value, expressed as total metal. Conversion to the dissolved form is made using the factor of 0.978 presented in U.S. EPA (1995a). U.S. EPA's Criterion Maximum Concentration (CMC) is equivalent to New York's Aquatic (Acute) value.

The reader will note that the attachment also derives U.S. EPA's chronic value, called a Criterion Continuous Concentration or CCC. This value is not presented in this fact sheet because New York's existing chronic aquatic standard for zinc is derived in a separate fact sheet.

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New York State Department of Environmental Conservation
Division of Water
SJS
January 28, 1997

ATTACHMENT

GREAT LAKES WATER QUALITY INITIATIVE

Tier 1 Aquatic Life Criterion for Zinc

The new acceptable acute data for zinc are given in Table P1; no new acceptable chronic data were found. These data were used with those given in Tables 1 and 2 of the criteria document for zinc (U.S. EPA 1987) to obtain the values given in Table P2. Because the toxicity of zinc is hardness-dependent, all acute values in Table P2 have been adjusted to a hardness of 50 mg/L.

Criterion Maximum Concentration (CMC)

The Final Acute Value (FAV) was calculated using the four lowest Genus Mean Acute Values in Table P2, resulting in an FAV of 133.2 ug/L at a hardness of 50 mg/L. This value did not need to be lowered to protect a commercially or recreationally important species of the Great Lakes System. The CMC was calculated by dividing the FAV by 2, resulting in a CMC of 66.6 ug/L, as total recoverable zinc, at a hardness of 50 mg/L. The CMC was related to hardness using the slope of 0.8473 that was derived in U.S. EPA (1987):

$$CMC = e^{0.8473(\ln \text{hardness}) + 0.884}$$

Criterion Continuous Concentration (CCC)

Insufficient chronic toxicity data were available to calculate a Final Chronic Value (FCV) using the eight-family procedure. Sufficient chronic data were available to calculate a FCV by dividing the FAV by the Final Acute-Chronic Ratio (FACR). SMACRs were available for seven species (Table P2), but three were for resistant species and one was a "less than" value. The other three were within a factor of 10.4. The FACR was calculated as the geometric mean of the three SMACRs and was 1.994. According to the GLI tier 1 methodology, the FACR cannot be less than 2. The FCV = FAV/FACR = (133.2 ug/L)/(2) = 66.6 ug/L at a hardness of 50 mg/L. This value did not need to be lowered to protect a commercially or recreationally important species of the Great Lakes System. Thus the CCC was 66.6 ug/L, as total recoverable zinc, at a hardness of 50 mg/L and equals the CMC. The CCC was related to hardness using the slope of 0.8473:

$$CCC = e^{0.8473(\ln \text{hardness}) + 0.884}$$

When it equals the CMC, the CCC is irrelevant because the CMC has a shorter averaging period.

The Criterion

The procedures described in the GLI tier 1 methodology indicate that, except possibly where a locally important species is very sensitive, aquatic organisms should not be affected unacceptably if the one-hour average concentration of zinc does not exceed the numerical value (in ug/L) given by the equation

$$CMC = e^{0.8473(\ln \text{hardness}) + 0.884}$$

more than once every three years on the average.

Table P1. New Acute Values for Zinc

Species	Method*	Hardness (mg/L as $CaCO_3$)	Acute Value (ug/L)	Adjusted Acute Value (ug/L)**	Reference
Frog, Xenopus laevis	S,M	100	34500	19176	Dawson et al. 1988
Cladoceran, Daphnia magna	S,U	300	1100	241	Berglind and Dave 1984

* S = Static, M = measured, U = unmeasured.

** Adjusted to a hardness of 50 mg/L using slope = 0.8473.

Table P2. Ranked Genus Mean Acute Values for Zinc.

Rank*	Genus Mean Acute Value (ug/L)**	Species	Species Mean Acute Value (ug/L)**	Species Mean Acute-Chronic Ratio
36	88960	Damselfly, *Argia* sp.	88960	-----
35	19800	Amphipod, *Crangonyx pseudogracilis*	19800	-----
34	19176	Frog, *Xenopus laevis*	19176	-----
33	18400	Worm, *Nais* sp.	18400	-----
32	17940	Banded killifish, *Fundulus diaphanus*	17940	-----
31	16820	Snail, *Amnicola* sp.	16820	-----
30	13630	American eel, *Anguilla rostrata*	13630	-----
29	10560	Pumpkinseed, *Lepomis gibbosus*	18790	-----
		Bluegill, *Lepomis macrochirus*	5937	-----
28	10250	Goldfish, *Carassius auratus*	10250	-----
27	9712	Worm, *Lumbriculus variegatus*	9712	-----
26	8157	Isopod, *Asellus bicrenata*	5731	-----
		Isopod, *Asellus communis*	11610	-----
25	8100	Amphipod, *Gammarus* sp.	8100	-----
24	7233	Common carp, *Cyprinus carpio*	7233	-----

Table P2. (Cont.)

Rank*	Genus Mean Acute Value (ug/L)**	Species	Species Mean Acute Value (ug/L)**	Species Mean Acute-Chronic Ratio
23	6580	Northern squawfish, Ptychocheilus oregonensis	6580	-----
22	6053	Guppy, Poecilia reticulata	6053	-----
21	6000	Golden shiner, Notemigonus crysoleucas	6000	-----
20	5228	White sucker, Catostomus commersoni	5228	-----
19	4900	Asiatic clam, Corbicula fluminea	4900	-----
18	4341	Southern platyfish, Xiphophorus maculatus	4341	-----
17	3830	Fathead minnow, Pimephales promelas	3830	5.644***
16	3265	Isopod, Lirceus alabamae	3265	-----
15	2176	Atlantic salmon, Salmo salar	2176	-----
14	2100	Brook trout, Salvelinus fontinalis	2100	2.335***
13	1707	Bryozoan, Lophopodella carteri	1707	-----
12	1672	Flagfish, Jordanella floridae	1672	41.2***
11	1607	Bryozoan, Plumatella emarginata	1607	-----
10	1578	Snail, Helisoma campanulatum	1578	-----
9	1353	Snail, Physa gyrina	1683	-----

Table P2. (Cont.)

Rank*	Genus Mean Acute Value (ug/L)**	Species	Species Mean Acute Value (ug/L)**	Species Mean Acute-Chronic Ratio
		Snail, *Physa heterostropha*	1088	-----
8	1307	Bryozoan, *Pectinatella magnifica*	1307	-----
7	>1264	Tubificid worm, *Limnodrilus hoffmeisteri*	>1264	-----
6	931.3	Rainbow trout, *Oncorhynchus mykiss*	689.3	1.554
		Coho salmon, *Oncorhynchus kisutch*	1628	-----
		Sockeye salmon, *Oncorhynchus nerka*	1502	<6.074***
		Chinook salmon, *Oncorhynchus tshawytscha*	446.4	0.7027
5	790	Mozambique tilapia, *Tilapia mossambica*	790	-----
4	299.8	Cladoceran, *Daphnia magna*	355.5	7.26
		Cladoceran, *Daphnia pulex*	252.9	-----
3	227.8	Longfin dace, *Agosia chrysogaster*	227.8	-----
2	119.4	Striped bass, *Morone saxatilis*	119.4	-----
1	93.95	Cladoceran, *Ceriodaphnia dubia*	174.1	-----
		Cladoceran, *Ceriodaphnia reticulata*	50.70	-----

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*   Ranked from most resistant to most sensitive based on Genus Mean Acute Value.

** At hardness = 50 mg/L.

*** Not used in the calculation of the Final Acute-Chronic Ratio.

At hardness = 50 mg/L:

FAV = 133.2 ug/L

CMC = FAV/2 = 66.6 ug/L

As a function of hardness:

$$CMC = e^{0.8473(\ln \text{hardness}) + 0.884}$$

FACR = 1.994 but was raised to 2

At hardness = 50 mg/L:

FCV = FAV/FACR = (133.2 ug/L)/(2) = 66.6 ug/L = CCC

As a function of hardness:

$$CCC = e^{0.8473(\ln \text{hardness}) + 0.884}$$